

TITLE: LOW EMISSION ETHANOL-DIESEL FUEL COMPOSITION

FIELD OF THE INVENTION

5 This invention relates to a stable diesel fuel-ethanol composition containing a surfactant and combustion improver and more particularly to a middle distillate fuel-ethanol composition which produces lower levels of vehicle emissions.

BACKGROUND OF THE INVENTION

10 This invention relates to a diesel fuel-ethanol composition, a method for preparing same employing a surfactant, a method for preparing a stable mixture of anhydrous ethanol and a diesel fuel that will remain stable under all field temperature and water contaminant conditions, and a water contaminated diesel fuel-ethanol composition. In one particular embodiment, the diesel fuel-ethanol composition further comprises a combustion improver and has the same or
15 similar performance as a pure middle distillate fuel.

 Using ethanol in gasoline is well established around the world. Traditionally, ethanol has not been used in middle distillate fuels, particularly because of compatibility difficulties arising from the presence of water.

20 The technology of mixing ethanol and middle distillate fuel has received much attention since the oil shortage crisis during the years between 1970 and 1980. However, ethanol-middle distillate fuel mixtures have suffered in a variety of performance areas: corrosion, reduced power, lubricity and low temperature properties. The corrosive properties of ethanol were traced back to the instability of this blend when exposed to contaminant water in the fuel delivery
25 system. This stability problem resulted in the fuel pump and injection equipment being exposed to high concentrations of ethanol and water. Moreover, this mixture suffered from reduced combustibility properties when compared to pure middle distillate fuel. The reduced combustibility is expressed as poorer start-up performance, reduced power and increased emissions. Reduced combustibility
30 can be attributed, at least in part, to the lower BTU content of ethanol versus middle distillate fuel.

Thus, while the use of ethanol in fuel systems offers economic and environmental advantages from a renewable fuel point of view, the presence of water creates difficult technical problems involving storage and use of such fuels. Even if a small quantity of water gets into the fuel, a fuel containing ethanol will
5 separate. The sources of this water can be the water that is difficult to remove from ethanol, or water that can be picked up by the fuel composition from the environment. The problems associated with phase stability, which refers to the ability of the fuel to refrain from separating into its component phases, can be addressed in principle by using either microemulsion or macroemulsion technology.
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Hybrid diesel fuel emulsions and micro emulsions have been developed to improve the water tolerance of diesel fuels. Such emulsions include, for example, a mixture of diesel fuel, an alcohol, small amounts of water, and a surfactant system. A number of patents, including U.S. Pat. Nos. 6,129,773; 6,348,074;
15 4,477,258; 4,451,265; and WO PCT Applications WO 01/10982 and WO 95/02654, describe surfactant systems containing long-chain fatty acids or derivatives thereof.

Various patents have published or issued which relate to emulsified fuel compositions and which specifically relate to compositions comprised of hydro-
20 carbon fuel, ethanol, and surfactant. In PCT Application WO 93/24593 and EP Application EP 01179715, higher alcohols (C3-C20) are used to impart phase stability. Typical alcohols used were propanol, butanol, hexanol, and dodecanol with butanol being the preferred higher alcohol.

The use of alkoxyated fatty alcohols and fatty acids as a stabilizing
25 additive for diesel fuel containing ethanol has been disclosed in U.S. Pat. Nos. 6,306,184; 6,190,427; 6,017,369; 6,348,074; PCT App. Nos. WO 00/36055; WO 01.62877; WO 01.62876; WO 01/44413; WO 01/10982; and U.S. Pat. App. No. 2001/000381.

While microemulsion and macroemulsion technologies provide a solution
30 to the stability problems associated with middle distillate-ethanol blends, they do not address the reduced combustibility properties when compared to pure middle distillate fuel.

5 The present invention provides for simple low cost stable diesel fuel-ethanol blends and solves the problem of increased emissions due to the presence of the ethanol in a diesel fuel such as a middle distillate fuel. When a combustion improver is employed, combustibility properties are restored to levels approaching that of a pure middle distillate fuel.

SUMMARY OF THE INVENTION

The present invention provides a fuel composition for use in a compression ignition engine that comprises

- (a) a diesel fuel,
- 10 (b) ethanol,
- (c) a surfactant, and
- (d) a combustion improver

wherein the fuel composition produces lower levels of regulated and unregulated engine exhaust emissions.

DETAILED DESCRIPTION OF THE INVENTION

15 As used herein, the terms "hydrocarbyl" and "hydrocarbon based" mean that the group being described has predominantly hydrocarbon character within the context of this invention. These include groups that are purely hydrocarbon in nature, that is, they contain only carbon and hydrogen. They may also include
20 groups in the hydrocarbon or attached to the hydrocarbon containing substituents or atoms that do not alter the predominantly hydrocarbon character of the group. Such substituents may include halo-, alkoxy-, nitro-, etc. These groups may also contain hetero atoms. Suitable hetero atoms will be apparent to those skilled in the art and include, for example, sulfur, nitrogen and oxygen. Therefore, while
25 remaining predominantly hydrocarbon in character within the context of this invention, these groups may contain atoms other than carbon present in a chain or ring otherwise composed of carbon atoms provided that they do not adversely affect reactivity or utility of the process or products of this invention.

30 In general, no more than about three non-hydrocarbon substituents or hetero atoms, and preferably no more than one, will be present for every 10 carbon atoms in the hydrocarbon or hydrocarbon based groups. Most preferably,

the groups are purely hydrocarbon in nature, that is, they are essentially free of atoms other than carbon and hydrogen.

Throughout the specification and claims the expression oil or fuel soluble or dispersible is used. By oil or fuel soluble or dispersible is meant that an amount needed to provide the desired level of activity or performance can be incorporated by being dissolved, dispersed or suspended in an oil of lubricating viscosity or fuel. Usually, this means that at least about 0.001% by weight of the material can be incorporated into a lubricating oil or fuel composition. For a further discussion of the terms oil or fuel soluble and dispersible, particularly “stably dispersible”, see U.S. Patent 4,320,019, expressly incorporated herein by reference for relevant teachings in this regard.

The expression “lower” is used throughout the specification and claims. As used herein to describe various groups, the expression “lower” is intended to mean groups containing no more than 7 carbon atoms, more often, no more than 4, frequently one or two carbon atoms.

It must be noted that as used in this specification and appended claims, the singular forms also include the plural unless the context clearly dictates otherwise. Thus the singular forms “a”, “an”, and “the” include the plural; for example “a fuel” includes mixtures of fuels of the same type. As another example, the singular form “oil” is intended to include both singular and plural unless the context clearly indicates otherwise.

The expression ‘a major amount’ refers to an amount greater than 50% of the whole, usually by weight or by volume relevant to the context or as expressly stated, and minor amounts are amounts less than 50%. When more than one component is present in a ‘minor amount’, in the aggregate they total less than a “major amount”.

Diesel Fuel

Component (a) is a diesel fuel which generally is present in the fuel composition of the present invention in a major amount. The diesel fuel can be a middle distillate fuel. Middle distillate fuels have boiling range temperatures greater than those of gasoline. The term "middle distillate" is intended to include the diesel, jet fuel, heating oil, gas oil and kerosene boiling range fractions.

The kerosene or jet fuel boiling point range is intended to refer to a temperature range of about 280°-525° F (138°-274° C) The term "diesel boiling range" is intended to refer to hydrocarbon boiling points of about 250°-700° F (121°-371° C). Gasoline or naphtha is normally the C₅ to 400° F (204° C) endpoint fraction of available hydrocarbons. The boiling point ranges of the various product fractions recovered in any particular refinery will vary with such factors as the characteristics of the crude oil source, refinery local markets, product prices, etc. Reference is made to ASTM standards D-975 and D-3699-83 for further details on kerosene and diesel properties.

The diesel fuel is typically a hydrocarbon based fuel. Hydrocarbon based fuels are those fuels that are substantially hydrocarbon. Hydrocarbon based fuels can be derived from mineral oil sources and can be a middle distillate fuel. The hydrocarbon based fuel can be derived from a synthetic process and can be a polyolefin fuel, an alkylated aromatic hydrocarbon fuel, or a Fischer-Tropsch fuel from the Fischer-Tropsch process.

Any diesel fuel meeting the requirements set forth in ASTM Procedure D-975 is useful in this invention and is preferred. The diesel fuel can be a hydrocarbon based fuel that is derived from animal fats or vegetable oils to include a biodiesel fuel.

Fischer-Tropsch fuels are derived from an indirect coal liquefaction process which first involves generation of synthesis gas by steam gasification of coal followed by production of hydrocarbons and oxygenates by catalytic reduction of CO in subsequent steps of the process (see Baldwin, Robert, "Coal Conversion Processes, Liquefaction" in Kirk-Othmer Encyclopedia of Chemical Technology (1993)).

Biodiesel fuels are biomass fuels are derived from organic materials, such as seeds. Processes for obtaining these oils from biomass are described in numerous U.S. Patents, many of which are listed in U.S. Patent 6,166,231 which is hereby incorporated herein by reference for relevant disclosures of such oils and methods for obtaining them.

As is well known to those skilled in the art, aromatic hydrocarbons in middle distillate fuels such as diesel oil represent a source of atmospheric pollu-

tion. The aromatic content of those middle distillates may be as high as 85 v %. Illustrative is a light straight run gas oil that typically can contain 30 v % aromatics. As environmental considerations become of greater concern, it is desirable to treat middle distillate hydrocarbons to decrease the content of undesirable aromatic components. While low aromatic content fuels are preferred, fuels containing high aromatic content are also within the scope of this invention.

In one embodiment, the diesel fuel is a middle distillate fuel and contains from about 5 to about 60% aromatic content as determined by ASTM Procedure D-5186. In another embodiment, the diesel fuel comprises a Fischer-Tropsch fuel. In yet another embodiment, the diesel fuel comprises a biodiesel fuel. In a further embodiment the diesel fuel is a mixture of two or more fuels taken from the group consisting of a middle distillate fuel, a Fischer-Tropsch fuel and a biodiesel fuel.

Several diesel fuels and several properties thereof are illustrated in Table

1.

Table 1. Diesel Fuel Properties

Fuel	Aromatic Content	Unsaturation Content	Sulfur, ppm	Temp for 90% distilled, °C	Cloud Pt. (ASTM D-2500)
A	20%	1.4%	282	298	-5°C
B	30%	1%	408	322	-18.4°C
C	21.8%	1.1%	104	334	-6.5°C
D	17.2%	1.7%	560	355	5.4°C
E	28.4%	1.3%	1750	359	-4.7°C
F	4.3%	0.3%	19	154	-21.2°C

Amounts of (a) the diesel fuel in the compositions of the present invention generally range from about 55% to about 99% by weight, or from about 70% to about 99% by weight, or from about 87% to about 95% by weight.

Ethanol

Component (b) is ethanol. As noted hereinabove, the use of ethanol in diesel fuel tends to reduce objectionable emissions and has the additional benefit

of being derived from renewable resources, for example, ethanol can be made by the fermentation of grain and/or sugar cane.

The ethanol may be anhydrous ethanol, fuel grade ethanol, hydrous ethanol, or mixtures thereof. For the purposes of this invention, anhydrous ethanol is defined as ethanol that is substantially free of water, that is, there is no more than a minor, impurity amount of water which has no significant measurable effect on performance or stability of a diesel fuel composition containing the ethanol. Anhydrous ethanol, as defined herein, may contain up to about 0.1% by weight water, frequently from about 0.01% to 0.1%, more preferably up to about 0.05% by weight of water. Fuel grade ethanol can contain up to about 0.1% by weight water. Hydrous ethanol contains more than the 0.1% upper amount specified for anhydrous ethanol, often up to about 7% by weight, more often up to about 3% by weight water.

Small amounts of water in anhydrous ethanol, as defined herein, frequently arise from unintentional contamination, such as by absorption from moist air. Greater amounts can arise from processing, for example from fermentation of grain yielding an azeotropic ethanol-water mixture.

The amount of ethanol in the compositions of the present invention may range from less than 1%, e.g., from about 0.5% by weight up to about 25%, often to about 20%, and more generally from about 3% to about 15%, preferably from about 5% to about 10% by weight.

Surfactant

Component (c) is a surfactant system that can impart stability to the fuel composition of the present invention that contains a diesel fuel-ethanol blend in the presence of small quantities of water.

Mixtures of diesel fuel and anhydrous ethanol, within the ranges for ethanol as defined hereinabove, are usually stable and require no stabilizer, surfactant or emulsifier. It is not until the diesel fuel-ethanol mixture is exposed to significant amounts of moisture and/or low temperatures that stability difficulties arise. The fuel composition of the present invention containing a surfactant and anhydrous ethanol is protected from such adverse effects when the composition is exposed to water and/or low temperatures.

In one instance, the fuel composition may be exposed to moisture from environmental sources. These sources include condensation from the atmosphere, accidental contamination, and other sources. To protect the diesel fuel-ethanol mixture, it is desirable to provide a means such that exposure of the diesel fuel-ethanol mixture to excessive amounts of water does not result in an adverse effect such as separation of ethanol from the diesel fuel.

In another embodiment, the ethanol may be a hydrous ethanol. In this embodiment, it is necessary that the fuel composition contains a component that prevents adverse effects arising from the presence of water in the hydrous ethanol

It has been found that including a surfactant in the fuel composition protects the diesel fuel-ethanol mixture from adverse effects arising from water contamination of anhydrous ethanol or from the use of hydrous ethanol.

Component (c) can be a surfactant having the general formula R-X wherein R is a hydrocarbyl group containing from about 4 to about 20 carbon atoms and X is a polar group. Preferred surfactants are those wherein X comprises a phenolic group or a derivative thereof, a carboxylic acid group or derivative thereof, an alcoholic group or derivative thereof, or mixtures thereof.

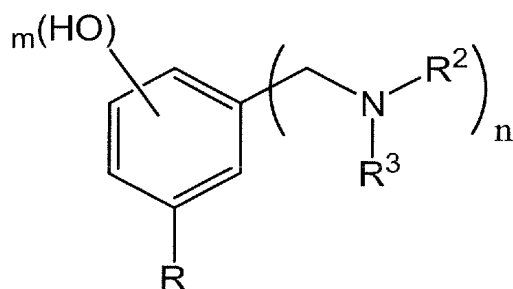
The group R is a hydrocarbyl group, preferably an aliphatic hydrocarbyl group. The R group may be alkyl or alkenyl. Illustrative R groups are butyl, heptyl, octyl, decyl, dodecyl, hexadecyl, oleyl, or mixtures thereof. These groups are often derived from aliphatic olefins such as butenes, heptenes, octenes, decenes, dodecenes, and particularly tetrapropylene oligomers. In other embodiments, the hydrocarbyl group is a fatty group, such as the hydrocarbon component of a fatty acid, for example, oleyl and stearyl.

In one preferred embodiment, the surfactant comprises a hydrocarbylphenol. Preferably, the hydrocarbyl group is an aliphatic group and is derived from an aliphatic olefin. The hydrocarbyl group contains from about 4 up to about 20 carbon atoms, preferably, from about 6, often from about 7 carbon atoms, up to about 15 carbon atoms, often up to about 12 carbon atoms. Many of the phenolic compounds useful as surfactants in this invention are commercially available. They are readily

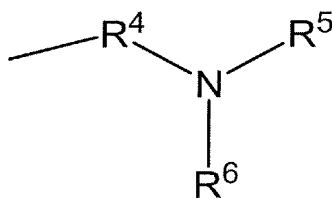
prepared by methods well known to those of skill in the art, such as by alkylation of phenol with an olefin, employing a Lewis acid catalyst.

In another preferred embodiment, the surfactant is a Mannich base of a hydrocarbyl phenol. Compounds of this type include those having the formula

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wherein R is an aliphatic hydrocarbyl group as described hereinabove; R² is hydrogen or a lower alkyl or hydroxy substituted lower alkyl radical; R³ is a hydroxy substituted lower alkyl radical or



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wherein R⁴ is a lower alkylene radical; R⁵ is hydrogen or a lower alkyl or hydroxy-substituted lower alkyl radical; R⁶ is a hydroxy-substituted lower alkyl radical; m = 1 or 2; and n = 1 or 2.

The surfactant can be a Mannich base of a hydrocarbyl phenol or a hydrocarbyl substituted hydroxyaromatic compound. Thus, the Mannich base may be derived from hydroxyaromatic compounds such as phenol, catechol, resorcinol, α-naphthol or β-naphthol. Alkyl substituted hydroxyaromatic compounds are particularly preferred, especially monoalkyl-substituted hydroxyaromatic compounds in which the alkyl group contains at least about 4 and preferably up to about 20 carbon atoms.

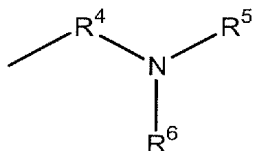
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An especially preferred compound for use as a surfactant in this invention is a Mannich base, as depicted in the formula hereinabove or derived from a hydrocarbyl substituted hydroxyaromatic compound as described above, in which the hydrocarbyl group or substituent is an alkyl group containing about 10-20 carbon atoms, and the Mannich base has one Mannich condensation group from the condensation reaction of

hydrocarbyl hydroxyaromatic compound, aldehyde or ketone compound, and an amine. The Mannich base is preferably a mono base having just one Mannich condensation group although it is possible to have as many Mannich condensation groups as the number of aromatic carbon atoms not otherwise substituted.

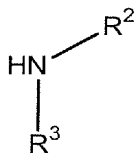
5 In a preferred Mannich base the Mannich nitrogen atom has two hydroxy-substituted lower alkyl groups each having 7 or less carbon atoms, especially where the hydroxy-substituted lower alkyl groups are hydroxyethyl groups. Alternatively where the Mannich nitrogen does not have a hydroxyalkyl group it is has a hydrogen or lower alkyl group. In a preferred embodiment of the invention the Mannich base is
10 the reaction product of dodecylphenol, formaldehyde, and diethanolamine.

Also contemplated for use as a surfactant in this invention are Mannich bases prepared from an amine which is an alkylenediamine or an alkoxyated alkylenediamine to include Mannich bases as depicted in the formula above where R³ is



15 wherein R⁴ is a lower alkylene (usually an ethylene) group; R⁵ is hydrogen or a lower alkyl or hydroxy-substituted lower alkyl group and is usually a hydroxyethyl group; and R⁶ is a hydroxy-substituted lower alkyl group and is usually a hydroxyethyl group. Compounds of this type can be derived from hydroxyalkyl-substituted alkylene diamines such as 2-(2-aminoethylamino)ethanol.

20 These Mannich bases are conveniently prepared by the Mannich reaction of a hydrocarbyl substituted hydroxyaromatic compound, formaldehyde or formaldehyde equivalent (e.g., paraformaldehyde, trioxane, dimethoxymethane), and an amine of the formula



25 wherein R² and R³ are defined as described hereinabove.

Also suitable for use as a surfactant of this invention are adducts of at least one epoxide with one or more Mannich bases as described above. The epoxides used for preparing the adduct may be for example, ethylene oxide, propylene oxide, and butylene oxide. Up to about 20 moles of epoxide can be used per mole of Mannich base.

In still another preferred embodiment, the surfactant comprises a hydrocarbyl substituted carboxylic acid or a derivative thereof. The hydrocarbyl group is preferably an aliphatic group. The hydrocarbyl group contains from about 4 to about 20 carbon atoms, preferably from about 6 to about 18 carbon atoms, and particularly from about 12 to about 18 carbon atoms. The carboxylic acids may be mono- or polycarboxylic acids, preferably mono- or dicarboxylic acids. Especially preferred are fatty monocarboxylic acids containing a total of from about 6 to about 18 carbon atoms, and aliphatic group substituted succinic acids and anhydrides thereof wherein the hydrocarbyl group contains from about 12 to about 18 carbon atoms. Particular examples include tall oil fatty acids, oleic acid, and octadecenylsuccinic acid or the anhydride thereof. These are all commercially available or may be readily prepared by methods known to those of skill in the art.

As noted hereinabove, derivatives of the carboxylic acids are also useful as surfactants. These derivatives include amides, imides, esters, amine salts, ester-amides, ester-amine salts, amide-amine salts, acid-amides, acid-esters and mixtures thereof. Especially preferred are succinic derivatives such as hydrocarbyl group substituted succinic acid or anhydride derivatives of amines, alkanolamines and alcohols wherein the hydrocarbyl group contains from about 6 to about 18 carbon atoms. These derivatives of hydrocarbyl substituted succinic acids or anhydrides can include imides, acid-amides, acid-esters, amides, amide-esters, amide-amine salts, esters, ester-amine salts, amine salts, and mixtures thereof. In an embodiment of the present invention the surfactant is an ester or ester-amine salt from the reaction product of an alkylsuccinic or alkenylsuccinic acid or anhydride thereof and an amino alcohol, and in a further embodiment the amine of this amino alcohol is a tertiary amine. These various carboxylic acid derivatives are readily prepared by methods well known to those skilled in the art. Examples of such methods include, but are not necessarily limited to, reac-

tion of the acid or an acyl halide or anhydride thereof with amines, alcohols, amino alcohols, or mixtures thereof. While salts generally form readily at ambient temperature, formation of esters, amides, imides and the like generally require the use of elevated temperatures. Methods for preparing the derivatives
5 are well known and do not constitute part of this invention.

Particularly useful carboxylic acid derivatives are the diethanolamides in which the nitrogen is substituted by an acyl substituent $RC(O)-$ having about 5-21 carbon atoms, preferably 7-19 carbon atoms, and more preferably 13-19 carbon atoms. The reaction products derived from the reaction of an alkanola-
10 mine with a fatty acid or a methyl or glyceryl ester of a fatty acid are especially useful. Illustrative fatty acids include pelargonic, oleic, linoleic, linolenic, erucic, and the free acid mixtures derived from natural triglycerides oils such as soybean, tall, safflower, sunflower, linseed, cottonseed, corn, palm, and rape-
seed.

15 Other useful carboxylic acid derivatives are esters derived from the herein-above described fatty acids and alcohols or polyols having from about 1 to about 8 carbon atoms and from 1 to about 6 oxygen atoms. Examples of such alcohols include methanol, ethanol, propanol, isopropanol, butanol, glycerol, sorbitol, penta-
erythritol and trimethylolpropane. In instances where the ester involves a polyol, at
20 least one up to all of the oxygen atoms can have a fatty acid group attached. Illustrative examples include triglycerides derived from vegetable oils such as soybean, corn, rapeseed, sesame, cottonseed, crambe, sunflower, peanut, linseed, safflower and palm.

A number of patents, including U.S. Pat. Nos. 6,129,773; 6,348,074; 4,477,258; 4,451,265; and WO PCT Applications WO 01/10982 and WO 95/02654,
25 describe surfactant systems containing long-chain fatty acids or derivatives thereof and are incorporated herein by reference.

In still another embodiment, hydrocarbyl alcohols useful as surfactants in the present invention can be selected from alcohols having chains that are saturated, unsaturated, or mixtures thereof and that are branched, straight, or mixtures thereof.
30 The hydrocarbyl group of the alcohol can have about 4 to about 20 carbon atoms, or about 6 to about 18 carbon atoms, or about 12 to about 18 carbon atoms. Particular examples include propanol, isopropyl alcohol, butanol, pentanol, octanol, decanol,

dodecanol, cetanol, isooctyl alcohol, and isononyl alcohol. These are all commercially available or may be readily prepared by methods known to those skilled in the art.

In PCT Application WO 93/24593 and EP Application EP 01179715, higher alcohols (C3-C20) are used to impart phase stability. Typical alcohols used were propanol, butanol, hexanol, and dodecanol with butanol being the preferred higher order alcohol.

In yet another embodiment, the hereinabove described hydrocarbyl phenol, hydrocarbyl substituted carboxylic acid or a derivative thereof, and hydrocarbyl alcohol can be further derivatized by reacting them with epoxides having from about 2 to about 4 carbon atoms. Illustrative epoxides include ethylene oxide, propylene oxide, butylene oxide, and mixtures thereof. The degree of alkoxylation, e.g., ethoxylation, propoxylation, butoxylation or alkoxylation from mixtures of epoxides may be from about 1 to about 50, or from about 1 to about 20, or from about 1 to about 10.

The use of alkoxyated fatty alcohols and fatty acids as a stabilizing surfactant for diesel fuel containing ethanol has been disclosed in U.S. Pat. Nos. 6,306,184; 6,190,427; 6,017,369; 6,348,074; PCT App. Nos. WO 00/36055; WO 01.62877; WO 01.62876; WO 01/44413; WO 01/10982; and U.S. Pat. App. No. 2001/000381.

In still yet another embodiment, the surfactant can comprise a ketal, acetal, or an orthoesters. The ketal may be characterized by the formula $(R^2)_2C(OR^3)_2$; the acetal may be characterized by the formula $R^2CH(OR^3)_2$ and the orthoesters may be characterized by the formula $R^2C(OR^3)_3$. In these compounds, R^2 or R^3 may be a hydrocarbon group to include alkyl and cycloalkyl groups. In the preferred embodiment, R^2 and R^3 may be lower alkyl i.e. C_1 to C_7 , or C_1 to C_4 . Illustrative ketals may include 2,2-dimethoxy propane, 2,2-dimethoxy butane, and 2,2-dimethoxy pentane. Illustrative acetals may include di-methoxy methane, 1,1-di-methoxy propane, and 1,1-diethoxy propane. Illustrative orthoesters may include ethyl orthoformate, methyl orthobutyrate, and n-propyl orthoacetate.

The surfactant of the present invention preferably has a certain hydrophilic-lipophilic balance (HLB) value which is determined using the method described by John C. McGowan in "A New Approach for the Calculation of HLB Values of

Surfactants,” *Tenside Surf. Det.*, 1990, 4, pp. 229-230. Preferred surfactants have HLB values ranging from about -30 to about 20, preferably from about -20 to about 10, and more preferably from about -15 to about 8 or about -7 to about 20. The aromatic content of the fuel frequently will indicate more useful HLB value ranges for the surfactant. Typically, the HLB value of the surfactant will be directly proportional to the aromatic content of the fuel- higher HLB value surfactants being used with diesel fuels containing high levels of aromatics and lower HLB value surfactants being used with diesel fuels having a lower aromatic content. Moreover, the treatment levels of surfactant are generally inversely proportional to the HLB value of the surfactant; that is, for a fuel having a given aromatic content, higher HLB value surfactants may be used in smaller amounts than lower HLB value surfactants.

Mixtures of surfactants may be used. One example of such a mixture of surfactants is the reaction product of hexadecenylsuccinic anhydride and N,N-dimethylethanolamine and the amine oleylamine in a ratio that delivers a HLB value of 5.6.

The amount of component (c) surfactant used in the fuel composition of the present invention generally ranges from about 0.1% to about 8% of surfactant having an HLB value between 10 to -30, preferably from about 0.5% to about 3% of surfactant having an HLB between 8 to -20, and more preferably from about 1% to about 2% of surfactant having an HLB value between 7 to -15.

Several surfactant compositions of this invention are illustrated in Table 2.

Table 2. Surfactant Compositions

Example	C ₇ Phenol	C ₁₂ Phenol	Tall Oil Fatty Acid	Oleic Acid	*	Other
1	90		5		5	
2	72		4		4	20 **
3		90	5		5	
4	80		10		10	
5		35		65		
6		50		50		
7				100		
8				50	50	
9						100***
10						100****
11	90					10*****
12	97.5		1.25		1.25	

* : C₁₆ succinic anhydride/N,N-dimethylethanolamine reaction product

** : 2-Ethyl Hexanol

*** : Tall Oil Fatty Acid/dimethylethanolamine reaction product

**** : Oleic acid/NH₃ reaction product

***** : Mannich Base of dodecylphenol and diethanolamine

Combustion Improver

As noted hereinabove, the inclusion of ethanol in a fuel composition tends to degrade the combustion performance of the base fuel. In some aspects, the degradation of performance is simply a proportional reduction of output or of fuel economy of the ethanol-containing fuel compared to the base fuel without ethanol. From time to time, the ethanol containing fuel may exhibit more undesirable effects such as poor start up characteristics, and the like. It has been discovered that incorporating materials which serve as combustion improvers enhances combustion characteristics of the fuel composition of the present invention to include producing lower levels of regulated and unregulated engine exhaust emissions, reducing engine noise, improving engine cold start, and increasing engine longevity as a consequence of reducing rapid pressure rise associated with poor combustion. Regulated emissions include hydrocarbons, carbon monoxide, nitrogen oxides, and particulate matter while unregulated emissions include carbonyls, formaldehyde, and acetaldehyde. Accordingly, the

fuel composition of the present invention includes (d) at least one combustion improver.

Component (d) is a combustion improver containing functional groups chosen from peroxides such as organic peroxides, nitrate esters such as the organic nitrate ester 2-ethylhexyl nitrate, nitro compounds such as the organic nitro compound nitromethane, nitrate compounds such as the inorganic nitrate ammonium nitrate, compounds having at least one strained ring group containing from 3 to 5 ring atoms, hydroxyl amines and salts of hydroxyl amines, and mixtures thereof. Additional examples of combustion improvers include 2,2-dinitropropane, hydroxyl ammonium nitrate, dicyclopropyl ketone, N,N-diethylhydroxylamine and N,N-diethylhydroxylamine nitrate.

The amount of component (d) in the fuel composition of the present invention is about 0.005% to about 10% by weight of the fuel composition, more often from about 0.05% to about 2% by weight, typically about 0.5 % by weight, and in another embodiment about 0.25% by weight.

In one embodiment of the present invention, the fuel composition contains at least one combustion improver which is an organic nitrate ester. The organic nitrate ester includes nitrate esters of substituted or unsubstituted aliphatic or cycloaliphatic alcohols which may be monohydric or polyhydric. Preferred organic nitrate esters are substituted or unsubstituted alkyl or cycloalkyl nitrates having up to about 10 carbon atoms, preferably from 2 to about 10 carbon atoms. The alkyl group may be either linear or branched, or a mixture of linear and branched alkyl groups. Specific examples of nitrate compounds suitable for use in the present invention include methyl nitrate, ethyl nitrate, n-propyl nitrate, isopropyl nitrate, allyl nitrate, n-butyl nitrate, isobutyl nitrate, sec-butyl nitrate, tert-butyl nitrate, n-amyl nitrate, isoamyl nitrate, 2-amyl nitrate, 3-amyl nitrate, tert-amyl nitrate, n-hexyl nitrate, n-heptyl nitrate, n-octyl nitrate, 2-ethylhexyl nitrate, sec-octyl nitrate, n-nonyl nitrate, n-decyl nitrate, cyclopentyl nitrate, cyclohexyl nitrate, methylcyclohexyl nitrate, and isopropylcyclohexyl nitrate. Also suitable are the nitrate esters of alkoxy substituted aliphatic alcohols such as 2-ethoxyethyl nitrate, 2-(2-ethoxyethoxy)ethyl nitrate, 1-methoxypropyl-2-nitrate, 4-ethoxybutyl nitrate, etc., as well as diol nitrates

such as 1,6-hexamethylene dinitrate. While not particularly preferred, the nitrate esters of higher alcohols may also be useful. Such higher alcohols tend to contain more than about 10 carbon atoms. Preferred are the organic nitrate esters that are alkyl nitrates having from about 5 to about 10 carbon atoms, most especially mixtures of primary amyl nitrates, mixtures of primary hexyl nitrates, and octyl nitrates such as 2-ethylhexyl nitrate.

The concentration of the combustion improver, such as an organic nitrate ester, in the fuel composition of the present invention can be any concentration sufficient to counteract the reduction in combustion performance caused by the addition of ethanol in the present diesel fuel-ethanol blended fuel compositions. Generally, addition of ethanol to fuel acts to lower the cetane number of the fuel. Lowering of cetane number results in ignition delay, which can be counteracted by the addition of a combustion improver. Embodiments of the present invention include the fuel composition containing about 0.05 to about 10% or about 0.05 to about 1% by weight of the combustion improver.

The fuel compositions of the present invention may contain other additives which are well known to those skilled in the art. These can include supplemental combustion improvers such as those mentioned hereinabove (cetane number improvers for diesel fuels such as alkyl nitrates), dyes, antioxidants such as hindered phenols, lubricity agents, cold flow improvers, dispersants, surfactants, rust inhibitors such as alkylated succinic acids and anhydrides and derivatives thereof, bacteriostatic agents, auxiliary dispersants and detergents, gum inhibitors, fluidizers, metal deactivators, demulsifiers, anti-icing agents, corrosion inhibitors, and the like. The fuel compositions of this invention may be lead-containing or lead-free fuels. Preferred are lead-free fuels.

Fuel compositions of this invention are prepared by mixing the various components in any order. More often, the diesel fuel is mixed with ethanol, the surfactant is then added, and then the combustion improver and any other components are added. Alternatively, the diesel fuel is mixed with the surfactant to which mixture is added ethanol, and then the combustion improver and any other components are added.

Several fuel compositions of this invention are illustrated in the following tables. It should be understood that these examples are solely for the purpose of illustration, and are not intended to be limiting of the scope of the invention.

Stability Data

5 Table 3. Stability data for Fuel + 10% Ethanol + % H₂O

Water %	Surfactant		Fuel	Lowest Stable Temperature	Cloud Point
	Example #	Weight %		-18°C, 0°C, 20°C	ASTM D-2500
0	None	0	A	None	25.5 °C
0.025	1	2.0	A	20 °C	8 °C
0.025	1	2.5	A	0 °C	1.5 °C
0.025	1	3.0	A	0 °C	-2.8 °C
0.025	6	3.0	A	20 °C	2.6 °C
0.025	7	3.0	A	20 °C	1.7 °C
0.025	8	3.0	A	20 °C	4.2 °C
0.05	1, 6	0.8	A	None	
0.01	1	3.74	A	20 °C	14.2 °C
0.01	3	3.74	A	20 °C	19.1 °C
0.01	3 (+ #)	3.74	A	20 °C	8.7 °C
0.3	1	5.5	A	20 °C	20.7 °C
0	None	0	B	None	17.7 °C
0.025	11	3.0	B	-18 °C	-20 °C
0.025	1	3.0	B	0 °C	-9 °C

#: 2-ethyl hexyl nitrate

Lubricity Data

Lubricity and wear are particular concerns with fuel compositions containing a diesel fuel and ethanol. Ethanol is recognized as a poor lubricity fluid with lower viscosity in comparison to most diesel fuels. Bench lubricity tests have been developed to predict the lubricity of fuels. A bench test allows for a quick and simple test method that can be used for product development and quality control. However, to be of value, these bench tests must be correlated with the actual lubricity performance of fuels as determined by field tests or

pump tests. There is evidence shown that certain bench tests are reported to correlate well with pump tests for normal diesel fuels.

One such lubricity bench test for fuel is the ASTM D6079 High Frequency Reciprocating Rig Test (HFRR). This test involves a ball on plate configuration, with the contacting surfaces submersed in the test fuel. The ball oscillates on the plate, resulting in a measurable wear scar. The design of the test was intended to maximize boundary lubrication conditions and minimize the effect of fuel viscosity. This test can be run at either 25°C or at the standard temperature of 60°C.

Several surfactant compositions of this invention, that improve lubricity of diesel fuel and ethanol blends, are illustrated in Table 4.

Table 4 Lubricity Data

Fuel	% Ethanol	%Water	Surfactant		Wear scar, mm	
			Example #	Weight %	HFRR @ 60°C	HFRR 25°C
BP Supreme	0	0	None	0	0.46	0.36
BP Supreme	10	0.2	11	2.5	0.377	0.29
BP Supreme	10	0	5	4.0		0.19
Haltermann	0	0	None	0	0.565	0.36
Haltermann	10	0.03	None	0	0.584	0.49
Haltermann	10	0.03	11	2.5	0.366	0.35
Haltermann	10	0.03	1	2.0	0.237	0.26
Haltermann	10	0.03	1	1.0	0.265	0.32
Haltermann	10	0.03	12	1.0	0.417	0.37

15 Emissions Data

Emission Test Results: The regulated emissions of HC (hydrocarbons), CO, NOx and PM (particulate matter) were measured using the US06 vehicle test procedure as described in the Code of Federal Regulations on a VW Jetta equipped with a 1.9 liter engine fueled with a base diesel fuel and two fuel blends containing the base diesel fuel, 10 wt % fuel grade ethanol, and 1 wt % of the surfactant of Example 1 which were respectively Blend A and Blend B where Blend B also contained 5200 ppm of the combustion improver 2-ethylhexyl nitrate. Unregulated emissions of carbonyls, formaldehyde and acetaldehyde were also measured for all three fuels.

Base diesel fuel properties are presented in Table 5.

Table 5. Base Diesel Fuel Properties

FUEL PROPERTY	UNITS	TEST METHOD	BASE DIESEL FUEL
Specific Gravity at 15.6 °C		ASTM D 4052	0.8285
Viscosity at 40°C	CST	ASTM D 445	2.55
Hydrocarbon Type	Volume %	ASTM D1319	
Aromatic			25.4
Olefins			2.1
Saturates			72.5
Pour point	°C	ASTM D97	-10
Cloud point	°C	ASTM D2500	0
Sulfur content	%wt	ASTM D4045	0
Distillation	% recovered	ASTM D 86	
T ₁₀			
T ₅₀			
T ₉₀			
T ₉₅			585
Cetane Number		ASTM D 613	43.2
Cetane Index		ASTM D 976	51.85

The changes in percent of regulated and unregulated emissions for Blend A and B relative to the base diesel fuel are given in Table 6. The general increase in regulated and unregulated emissions, with the exception of particulate matter, in Blend A when ethanol is introduced into the diesel fuel can be explained as a result of ethanol lowering the cetane number of the fuel. A lower cetane number results in delayed ignition of the fuel and consequently poorer combustion and higher emissions. The unregulated emissions of carbonyl compounds are largely a result of poor combustion of ethanol itself. The delayed ignition can be counteracted by introducing a combustion improver to the diesel fuel-ethanol fuel blend. The emissions data for Blend B, in which there was a significant reduction in both regulated and unregulated emissions, clearly demonstrate the advantage of including a combustion improver in a diesel fuel-ethanol fuel blend.

Table 6: Emissions From Diesel Fuel-Ethanol Blend With Or Without Combustion Improver Relative To Base Diesel Fuel

Emissions Measurement	% Change in Emissions Relative to Base Diesel Fuel	
	Blend A without Combustion Improver	Blend B with Combustion Improver
HC	11.6%	4.2%
NOx	19.5%	12.4%
CO	19.8%	-7.3%
PM	-17.1%	-19.7%
Carbonyls	35.8%	4.1%
Formaldehyde	28.3%	3.6%
Acetaldehyde	64.3%	15.2%

It is known that some of the materials described above may interact in the final formulation, so that the components of the final formulation may be different from those that are initially added. For instance, metal ions (of, e.g., a detergent) can migrate to other acidic sites of other molecules. The products formed thereby, including the products formed upon employing the composition of the present invention in its intended use, may not be susceptible of easy description. Nevertheless, all such modifications and reaction products are included within the scope of the present invention; the present invention encompasses the composition prepared by admixing the components described above.

Each of the documents referred to above is incorporated herein by reference. Except in the examples, or where otherwise explicitly indicated, all numerical quantities in this description specifying amounts of materials, reaction conditions, molecular weights, number of carbon atoms, and the like, are to be understood as modified by the word "about." Unless otherwise indicated, each chemical or composition referred to herein should be interpreted as being a commercial grade material which may contain the isomers, by-products, derivatives, and other such materials which are normally understood to be present in the commercial grade. However, the amount of each chemical component is presented exclusive of any solvent or diluent oil which may be customarily present in the commercial material, unless otherwise indicated. It is to be understood that the upper and lower amount, range, and ratio limits set forth herein may be independently combined. As used herein, the expression "consisting

essentially of” permits the inclusion of substances which do not materially affect the basic and novel characteristics of the composition under consideration.

While the invention has been explained in relation to its preferred embodiments, it is to be understood that various modifications thereof will
5 become apparent to those skilled in the art upon reading the specification. Therefore, it is to be understood that the invention disclosed herein is intended to cover such modifications that fall within the scope of the appended claims.